Chemical equilibrium in a heterogeneous fluid phase system: thermodynamic regularities and topology of phase diagrams

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Singularities of the systems with simultaneous phase and chemical equilibria were examined. The thermodynamic regularities were revealed and topology of phase diagrams was presented for multicomponent heterogeneous systems including two or several equilibrium liquid phases (solution layering). The thermodynamic conditions for displacement of phase and chemical equilibrium are considered.

Key words: chemical and phase equilibrium, topology of diagrams, thermodynamics.

Real physicochemical systems are sophisticated and affected by a combination of various internal and external factors. The systems in which the phase and chemical processes occur simultaneously are among the most important and frequently studied objects. Interest in studying similar objects, *i.e.*, heterogeneous systems with interaction, is not purely academic. Simultaneously occurring phase and chemical processes are especially interesting for such areas as technology of heavy organic synthesis or separation of substances. A combination of the chemical reaction with simultaneous phase separation makes it possible to optimize the technological process towards energy and resource economy and to enhance ecological safety of the technology. Similar combined processes represent a type of reactive mass-transfer processes. For example, reactive distillation (or distillation rectification), when chemical synthesis is accompanied by the vapor—liquid phase transition, is practically significant.[1—5] Such reactive mass-transfer processes as reactive extraction or chemical synthesis in a membrane reactor are also technologically significant. At the same time, the phase transition occurring during the chemical reaction can play a negative role in technology. For example, when an initially homogeneous solution is layered during the reaction, the synthesis process is impeded. On developing the technology of organic synthesis, the choice of initial reactant concentrations are often dictated by the need to avoid undesirable phase transformations due to which the reaction mixture becomes heterogeneous. Therefore, information on the structure of phase diagrams of the reaction system is very important. Basic research into combined reactive mass-transfer processes and equilibrium states with simultaneous chemical and phase equilibrium allows one to establish new thermodynamic and kinetic regularities. In particular, the following new singularities were observed when studying the vapor—liquid phase transitions in the systems with chemical reactions: reactive azeotrope (or chemiazeotrope),[6—8] kinetic azeotrope,[9] and others. The full characterization of the topological structure of phase diagrams of reactive systems can include such singularities as the shape of reactive (or stiochiometric) lines, arrangement of varieties of chemical equilibria, and constancy of chemical affinity (isoaffinic varieties).[10—12] In this respect, the vapor—liquid systems in which chemical reactions occur are among the most studied fluid mixtures.[1,4,13,14]

In this review, we consider the main singularities of the topological structure of phase diagrams of liquid phase heterogeneous systems (*i.e.*, the systems including two or more liquid phases) related to chemical reactions. In addition, the thermodynamic regularities due to the simultaneous attainment of phase and chemical equilibria and their displacement in these systems were examined. The review includes our results and analysis of literature data on the liquid phase systems in chemical reactions complicated by layering.

Varieties of chemical equilibrium and reactive lines

We can focus now on the main concepts on elements of phase diagrams of multicomponent systems related to the occurrence of the chemical reaction. Reactive or stiochiometric lines reflect the displacement of the reaction mixture composition during the reaction. Their arrangement in the concentration area is uniquely specified by the stoichiometric equation of the chemical reaction. Figure 1 presents two variants of arrangement of reactive lines in the case of reactions in the system of three substances:

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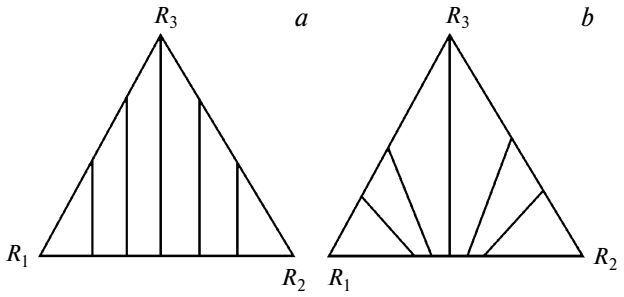

Fig. 1. Reactive lines in a system of three substances in the composition triangle: *a*, reaction $R_1 + R_2 = R_3$; *b*, reaction $R_1 + R_2 = 2\ R_3$.

$R_1 + R_2 = R_3$ (Fig. 1, *a*) and $R_1 + R_2 = 2\ R_3$ (Fig. 1, *b*), where R_i is the symbol of a substance.

In the general case of the multicomponent system with n substances, the displacement of the reaction mixture composition due to the reaction is described as follows:

$$(\mathrm{d}x_i^{(1)})_{\mathrm{react}} = \frac{\nu_i - x_i^{(1)} \sum_{j=1}^{n} \nu_j}{\nu_k - x_k^{(1)} \sum_{j=1}^{n} \nu_j} \mathrm{d}x_k^{(1)}, \qquad (1)$$

where x is the molar fraction of a component of the n-component system, ν are stiochiometric coefficients (they are positive for the reaction products and negative for the reactants), subscript is the index of a component, superscript is the phase index, and index "react" indicates that the chemical reaction is considered. Equation (1) is a mass balance equation during the chemical reaction in the system of n substances

$$\sum_{i=1}^{n} \nu_i R_i = 0 \qquad (2)$$

and can be considered as an equation of reacvive line. This equation can be obtained by the following transformations (for phase r)[12]:

$$\frac{\mathrm{d}m_1}{\nu_1} = \frac{\mathrm{d}m_2}{\nu_2} \ldots = \frac{\mathrm{d}m_i}{\nu_i},$$

$$\mathrm{d}m = \sum_{j=1}^{n} \mathrm{d}m_j = \frac{\mathrm{d}m_i}{\nu_i} \sum_{k=1}^{n} \nu_k,$$

$$\mathrm{d}m_i = m\mathrm{d}x_i + x_i\mathrm{d}m = \frac{\nu_i}{\sum_{k=1}^{n} \nu_k} \mathrm{d}m,$$

whence

$$\frac{dx_i^{(r)}}{\mathrm{d}\ln m^{(r)}} = \frac{\nu_i}{\sum_{k=1}^{n} \nu_k} - x_i^{(r)} \quad (i = 1, 2, \ldots, n), \qquad (3)$$

where $m^{(1)}$ is the number of moles of the phase. For reactions in which the total number of moles is fixed, *i.e.*,

$$\sum_{k=1}^{n} \nu_k = 0,$$

the derivative with respect to the total number of moles (m) in the left-hand part of Eq. (3) is meaningless. Total mass m, which is not a variable of the state, can be excluded by combining two Eqs (3) for substances i and k. Thus, we have Eq. (4) or another form of the equation of reactive curve having a clear geometric interpretation

$$\frac{dx_i^{(r)}}{dx_k^{(r)}} = \frac{\nu_i - x_i^{(r)} \sum_{j=1}^{n} \nu_j}{\nu_k - x_k^{(r)} \sum_{j=1}^{n} \nu_j} \qquad (i, k = 1, 2, \ldots, n). \qquad (4)$$

Unlike Eq. (3), which can simultaneously take zero value for all n components, the right-hand part of Eq. (4) does not simultaneously vanish for all $i = 1, 2,\ldots, n$. For the case presented, *e.g.*, in Fig. 1, *b*, the equation of reactive line (4) takes the following simple form:

$$\frac{\mathrm{d}x_1}{\mathrm{d}x_2} = 1 \text{ or } \frac{\mathrm{d}x_3}{\mathrm{d}x_2} = 2.$$

Let us briefly consider how the chemical equilibrium states can be described. The general conditions of chemical equilibrium are well known.[15–18] If one reaction occurs in the n-component system, a condition for the chemical equilibrium is

$$A = -\sum_{i=1}^{n} \nu_i \mu_i = 0, \qquad (5)$$

where A is affinity, and μ_i is the chemical potential of substance i. The point (under isothermic—isobaric conditions) or curve (under isothermic or isobaric conditions) in the area formed by the "composition—pressure" or "composition—temperature" variables, respectively, corresponds to the chemical equilibrium of the reaction between two substances

$$\sum_{i=1}^{2} \nu_i R_i = 0.$$

When temperature or pressure are varied, the area in the space of variables "composition—temperature—pressure" corresponds to the chemical equilibrium of this reaction. Hereinafter we confine our consideration to the set of thermodynamic variables corresponding to the fundamental Gibbs equation

$$U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{n} \nu_i \mathrm{d}m_i,$$

where U is the internal energy; T, S, P, V, and m_i are the temperature, entropy, pressure, volume, and amount of substance i, respectively. Hereinafter, we consider only the results of transformation of this equation for other

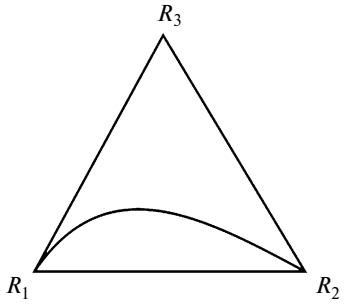

Fig. 2. Chemical equilibrium curve in the composition triangle: the reaction in a system of three substances.

thermodynamic potentials (Legendre transforms), including those in the concentration form.

The curve in the concentration triangle (Fig. 2) corresponds to the chemical equilibrium between three substances under the isothermic—isobaric conditions. When T or P is varied, the equilibrium is presented by the surface in the three-dimensional space "composition—T—P"; at variable T and P, the hypersurface in the four-dimensional space corresponds to the chemical equilibrium.

Finally, in the case of the reaction between four substances, the states of chemical equilibrium at T, P = const can be described by a surface in the concentration tetrahedron. The typical view of this surface in an irregular tetrahedron (in the rectangular Cartesian coordinates) is shown in Fig. 3. At variable pressure and (or) temperature, the hypersurface in the corresponding thermodynamic space corresponds to the chemical equilibrium. The cases of a higher number of substances are considered similarly.

The arrangement of isoaffinic varieties, *viz.*, curves, surfaces, and hypersurfaces at the constancy of affinity,

$$A = -\sum_{i=1}^{n} \nu_i \mu_i = \text{const}$$

is analogous in concentration simplexes, because the states corresponding to the non-zero affinity are attained due to

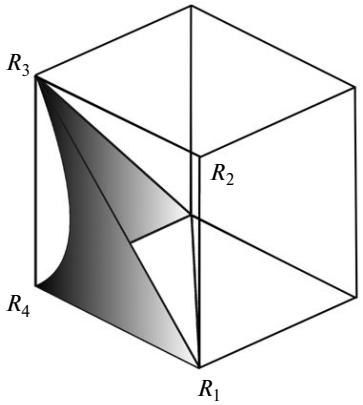

Fig. 3. Chemical equilibrium surface in the concentration tetrahedron.

the displacement from the equilibrium state. These varieties can graphically be presented as a result of "displacement" of the equilibrium curve or surface in the concentration space (composition triangle or tetrahedron).

Since it was difficult and evidently inconvenient to present chemical equilibrium varieties of multicomponent systems, the so-called transformed concentration variables were introduced. Thermodynamic derivation of fundamental equations in these variables (α variables) was proposed.[19] The number of concentration variables can be reduced, because the number of thermodynamic degrees of freedom is reduced by one for conditions for the chemical equilibrium (Eq. (5)). The introduction and variants of application of new composition variables were reliably substantiated.[6,19—22] Later almost the same transformed concentration variables were proposed on the basis of material balance equations.[23] For the system of four substances in the reaction

$$R_1 + R_2 = R_3 + R_4$$

(absolute values of all stoichiometric coefficients are equal to unity), new concentration variables take the form

$$\alpha_1 = x_1 + x_4,$$

$$\alpha_2 = x_2 + x_4,$$

$$\alpha_3 = x_3 - x_4.$$

Esterification, *viz.*, the synthesis (hydrolysis) of ester, can be a specific example of a similar reaction. Obviously, the α-variables are related as follows:

$$\alpha_1 + \alpha_2 + \alpha_3 = 1,$$

and they can take values in the ranges

$$0 < \alpha_1 < 1,$$

$$0 < \alpha_2 < 1,$$

$$-1 < \alpha_3 < 1.$$

In this case, the concentration space is a square of α-variables; *i.e.*, the equilibrium properties of the system can be presented on the basis of a binary complex of composition instead of the ternary concentration simplex. Possibilities of the use of transformed concentration variables in the case of the liquid phase heterogeneous reaction system will be illustrated below by specific examples.

Chemical equilibrium in the heterogeneous system the phase rule

As known,[15—17,24—26] in the case of simultaneous phase and chemical equilibrium (k reversible chemical reactions), the phase rule has the form

$$f = n + 2 - r - k, \quad (6)$$

where f is the number of degrees of freedom, n is the number of components (substances), r is the number of phases, and k is the number of reversible chemical reactions (*i.e.*, chemical equilibria).

Let us consider what consequences follow from the phase rule for the chemical and phase equilibria simultaneously existing in a heterogeneous system. For two liquid phases,

$$f = n + 2 - r - k = n + 2 - 2 - 1 = n - 1. \quad (7)$$

Then at altering pressure and temperature the binary system in the state of simultaneous phase and chemical equilibrium has one degree of freedom (monovariant equilibrium), the ternary system has two degrees of freedom (bivariant equilibrium), and the quaternary system has three degrees of freedom (polyvariant equilibrium). Correspondingly, at fixed T and P the simultaneous phase and chemical equilibrium in the binary system corresponds to the negative number of degrees of freedom *i.e.*, this should not be considered (as physically meaningless). At a variable temperature and P = const (or at a variable pressure and a fixed temperature) the non-variant state takes place (f = 0): a point in the thermodynamic "composition—temperature" (or "composition—pressure") space. Similarly, the ternary system at fixed T and P and simultaneous chemical and phase equilibrium exists in the non-variant state (the point in the composition triangle), whereas the quaternary system exists in the monovariant state (the curve in the composition tetrahedron).

Let us consider a special case: a possibility of the critical equilibrium state of two liquid phases. In the critical state the number of degrees of freedom is additionally reduced by one: $f = 3$ corresponds to the critical phase in Eq. (7).[15,17,24] Whence, in the quaternary system without a reaction (or in the chemically non-equilibrium state of the reaction system) data for these states at fixed T and P should be presented as a curve in the concentration tetrahedron. In the case of one equilibrium chemical reaction, for the critical phase (critical state of the two-phase equilibrium) it follows from Eq. (7) that

$$f = n + 2 - r - k = n + 2 - 3 - 1 = n - 2; \quad (8)$$

whereas for the isothermic isobaric conditions,

$$f = (n + 2 - r - k) - 2 = \\ = (n + 2 - 3 - 1) - 2 = n - 4. \quad (9)$$

Therefore, at fixed T and P the critical phase of the quaternary two-phase system in the chemical equilibrium state (one equilibrium reaction) exists in the non-variant state. Similar simultaneous equilibrium of the critical phase in systems with a lower number of components under isothermic isobaric conditions should not be considered ("negative" variance of the system). These problems have been addressed in more detail previously.[27]

Topology of diagrams of simultaneous chemical and phase equilibrium of ternary liquid—liquid systems

The consideration of topological singularities of diagrams of chemically equilibrium heterogeneous systems can be started from ternary systems. The case of binary systems is relatively simple.[27] An analysis of mutual arrangement of these equilibria in the thermodynamic space is a main issue in the problem related to the simultaneous chemical and phase equilibrium of the heterogeneous system. In the case of ternary system, we shall confine our consideration to the isothermic isobaric conditions and some types of diagrams describing the liquid—liquid equilibrium. In spite of these restrictions, the analysis performed below provides the main specific features of the topology of phase diagrams of the chemically reacting system during solution layering. We will proceed from the earlier analysis of possible variants of diagrams with intersection of the chemical equilibrium curves and binodals in ternary systems. Complete thermodynamic studies of the behavior of the chemically reacting ternary mixture are few. Among them there are works containing data on the complete construction of the chemical equilibrium curve (for a homogeneous solution).[28] The most part of studies of systems with layering are related to quaternary systems rather than to ternary.[13] Therefore, the discussion of the main types of topological structures of the diagrams on the basis of the available data[29] is mainly theoretical.

Let us consider a reversible chemical reaction

$$\nu_1 R_1 + \nu_2 R_2 = \nu_3 R_3, \quad (10)$$

occurring in the ternary liquid—liquid system, where substances R_1 and R_2 are taken to be reactants (for certainty) and R_3 is the reaction product. At fixed T and P isoaffinic varieties (*i.e.*, lines, surfaces. and hypersurfaces of chemical affinity constancy), including those for chemical equilibrium, are curves in similar ternary systems, as indicated above (for instance, in the coordinates "composition—chemical affinity" equilibrium is described by a curve in the space, and the curve on the plane is obtained in the projection on the concentration triangle). The affinity isoline corresponding to equilibrium

$$A = -\nu_1\mu_1 - \nu_2\mu_2 + \nu_3\mu_3 = 0, \quad (11)$$

passes through apices R_1 and R_2 of the composition triangle. Following Ref. 29, we consider some variants of mutual arrangement of the line of coexistence of two liquid phases: the binodal and the chemical equilibrium curve.

(1) A binary system R_1—R_3 ("reactant + product") undergoes layering, and point of intersection of the chemical equilibrium curve and binodal lie on different sides from

the critical point of liquid—liquid equilibrium. The tie-line, *i.e.*, the line segment connecting the intersection points, corresponds to the simultaneous chemical equilibrium and liquid—liquid equilibria. The corresponding diagram is presented in Fig. 4, *a*.

(2) A binary system R_1—R_3 undergoes layering, but the points of intersection of the chemical equilibrium line and binodal lie on one side from the critical point. In this case, there are two tie-lines points of which corresponds to the chemical and phase equilibrium conditions and the chemical equilibrium curve (in homogeneous regions) is divided into three local segments (see Fig. 4, *b*).

(3) A binary system consisting of reactants R_1—R_2 undergoes layering, and the intersection points of the chemical equilibrium line and binodal lie on different sides from the critical point. On the tie-line connecting these points the conditions of chemical equilibrium and liquid—liquid phase equilibrium are fulfilled (Fig. 4, *c*).

(4) A binary system consisting of reactants R_1—R_2 undergoes layering, and the intersection points of the chemical equilibrium line and binodal lie on one side from the critical point. In this case, two tie-lines satisfy the conditions of the phase and chemical equilibria, and the chemical equilibrium curve is divided into three segments (see Fig. 4, *d*).

(5) Two binary systems undergo layering with one of which consisting of reactants (R_1—R_2). The phase diagram of the ternary system contains a continuous layering region as a "band" extending from one binary subsystem to another (no critical points). The chemical equilibrium (as in the cases (1) and (3)) occurs as states, which in the phase diagram correspond to two sections of the chemical equilibrium curve connected by the liquid—liquid tie-line. In the case considered (unlike other cases), intersection of the chemical equilibrium line and the binodal necessarily occurs (see Fig. 4, *e*).

(6) Two binary systems undergo layering, and each of them includes the product and one of the reactants: systems R_1—R_3 and R_2—R_3. As in the case (5), the ternary system includes a continuous layering band. In this case, the system contains two liquid—liquid tie-lines on which the chemical equilibrium condition was fulfilled (see Fig. 4, *e*).

In all considered variants of the phase behavior of the chemical reactive mixture with layering, one (see Fig. 4, *a*, *c*, *e*) or two (see Fig. 4, *b*, *d*, *f*) tie-lines connect the parts of the chemical equilibrium curves. These tie-lines were defined as "unique reactive tie-lines." [30,31]

In addition to the variants presented above, other variants are possible, including special cases of mutual arrangement of the chemical and phase equilibrium curves in a system of three substances with the chemical reaction between them. Some example, such as mutual contact of the curves outlined above, and metastable and critical states were described.[27,29] The case of equilibrium of three liquid phases in the ternary system was also considered.[29] At fixed T and P, according to the phase rule, the three-phase equilibrium is incompatible with the chemical equilibrium condition for reaction (10).

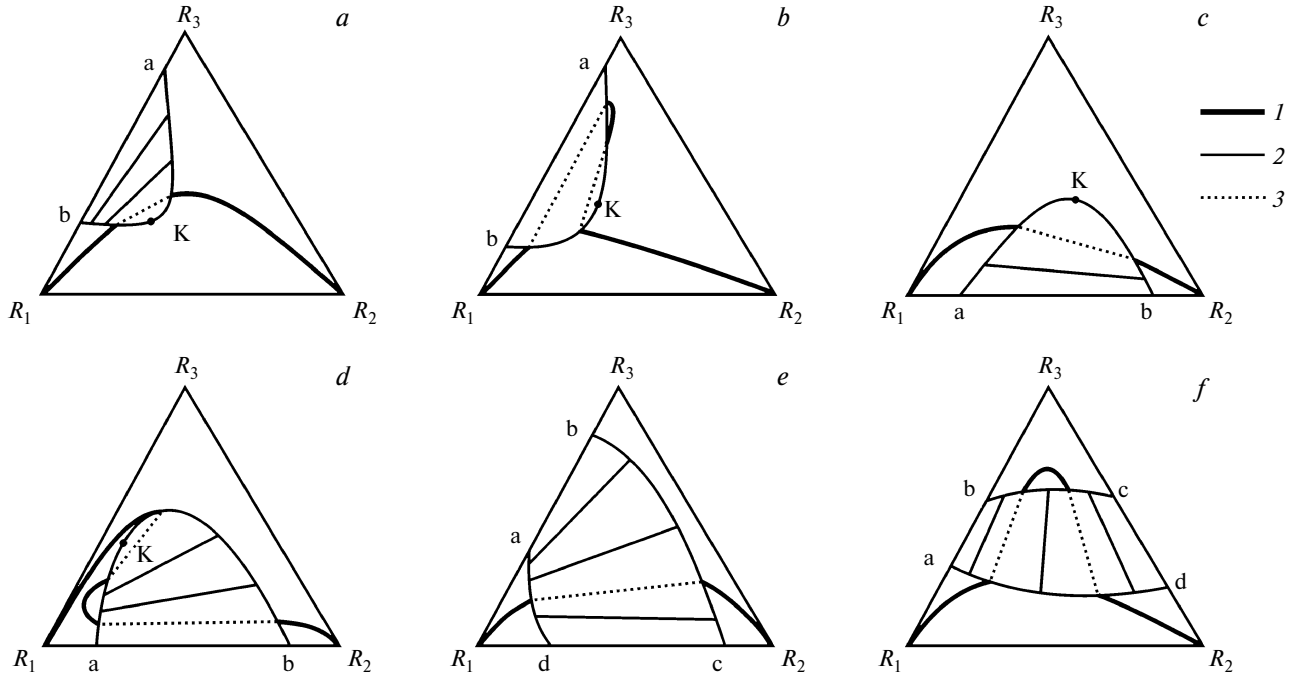

Fig. 4. Variants of mutual arrangement of the chemical equilibrium curves (*1*) and binodals (*2*) in the concentration triangle; *3*, unique reactive tie-line; K is the critical point; ab and dc are the solubility boundaries in the binary system.

Topological singularities of diagrams with simultaneous chemical and phase equilibrium in quaternary liquid—liquid systems

Much more variants of diagrams with simultaneous chemical and phase equilibria can be considered for quaternary systems with solution layering. Therefore, we shall confine our consideration to a relatively simple but important type of systems with restricted solubility in one of the binary subsystems and, as a consequence, in two ternary subsystems with layering regions.

Among practically important examples for such systems are systems with esterification

$$Alcohol\ (R_1) + Acid\ (R_2) = Water\ (R_3) + Ester\ (R_4). \qquad (12)$$

It is for these systems the absolute majority of experimental data on the phase equilibrium in systems with chemical reactions was obtained to date.[13,32] Because of restricted solubility of water and ester, the phase diagrams of quaternary systems alcohol—acid—water—ester usually include the layering region. At the same time, the most part of studies of these reaction systems (almost all experimental data) concern homogeneous regions of solution compositions. This is due to the fact that the main purpose of these studies was the determination of the vapor—liquid equilibrium (see, *e.g.*, Refs 4, 5, 13, and 33—39). Only several experimental works contain the data on phase processes in reaction systems in the regions with restricted miscibility of components. Among these studies is the work presenting the diagram with curves describing open evaporation in the system lauric acid—*n*-propanol—*n*-propyl laurate—water, including the layering region.[40] A majority of other studies devoted to phase transitions in liquid—liquid systems that occur during chemical reactions is related to general theoretical problems and simulation (see, *e.g.*, Refs 4 and 41—43).

Several possible explanations can be proposed for the restricted character of thermodynamic data on solubility in systems with chemical reactions, including the esterification reaction: the chemical equilibrium of esterification usually occurs in the homogeneous region of solution concentrations; the results of chemical equilibrium determination (in particular, belonging to the homogeneous region only) can be due to experimental errors.

Difficulties of experimental determination are caused by a complex character of the behavior of the chemically reacting heterogeneous liquid—liquid system in which three processes occur simultaneously: the phase transition and chemical reactions in two liquid phases. The rate needed to attain the liquid—liquid equilibrium can be of the same order of magnitude as that of the chemical equilibrium. In addition, the reaction rates in different phases (in the case of esterification, in "aqueous" and in "organic" phases) can be substantially different. Certain interest in the liquid—liquid reaction system is also caused by these difficulties: their further experimental study can result in the establishment of new phenomena and effects in the field of the theory of combined processes.

At constant temperature and pressure, the chemical equilibrium surface of reversible reaction (12) can graphically be represented in the composition tetrahedron (see Fig. 3). According to the equation of reaction (12), all the four ternary subsystems of the quaternary system exist only in the chemically nonequilibrium state. Two binary systems, namely, R_1—R_2 and R_3—R_4, "acid—alcohol" and "water—ester" are also chemically at nonequilibrium conditions and, hence, the chemical equilibrium surface cannot belong to the faces and edges of the concentration tetrahedron corresponding to the indicated ternary and binary systems. No chemical reaction occurs in four other binary subsystems (R_1—R_3, R_1—R_4, R_2—R_3, and R_2—R_4) and, therefore, the corresponding faces of the concentration tetrahedrom should be considered as boundaries of the chemical equilibrium surface. The same concerns the apices of the tetrahedron: the points of the composition of neat substances. Thus, the chemical equilibrium surface is localized inside the composition tetrahedron and is based in four edges corresponding to binary systems without chemical reactions.

Let us consider the experimental data on the chemical equilibrium and solubility in two systems formed by the products and reactants of the synthesis of ethyl acetate and *n*-propyl acetate. The experimental data on the chemical equilibrium in the acetic acid—*n*-propanol—water—*n*-propyl acetate system were obtained[44,45] for 313.15 K. The vapor—liquid equilibrium was studied in the same works; thermodynamic tests and discussion of the results were described in several works.[46,47] The chemical equilibrium was experimentally studied and the arrangement of the chemical equilibrium surfaces in the concentration tetrahedron was presented at 303.15 and 293.15 K (see Refs 48—50). The detailed experimental study of solubility and liquid—liquid equilibrium at 313.15, 303.15, and 293.15 K in the quaternary system was published.[48,51] The solubility and equilibria of the liquid phases in the both layering ternary systems (acetic acid—water—*n*-propyl acetate and *n*-propanol—water—*n*-propyl acetate) were studied.[45,48,52—59] The chemical equilibrium surface constructed on the basis of experimental data is shown in Fig. 5, and the layering surface (binodal surface) is shown in Fig. 6 (for 293.15 K). It was revealed by the performed experimental study that the chemical equilibrium of *n*-propyl acetate synthesis is established not only in the homogeneous but also in the heterogeneous range of compositions at all three temperatures indicated. This means that the chemical equilibrium and layering surfaces have a region of mutual intersection in the composition tetrahedron. Results of combination of the both

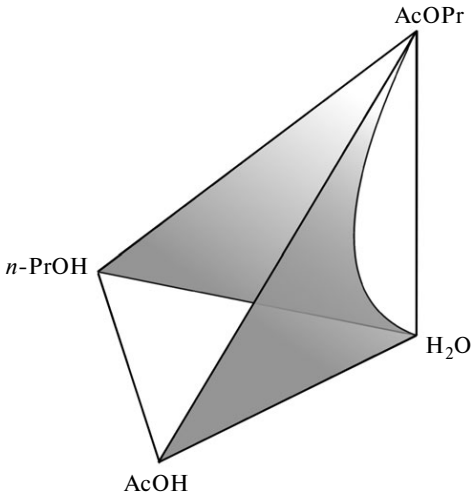

Fig. 5. Chemical equilibrium surface in the system acetic acid—*n*-propanol—water—*n*-propyl acetate at 293.15 K.

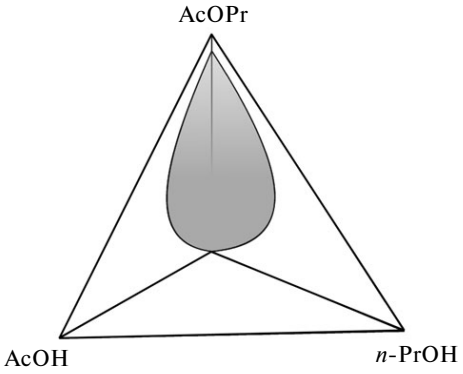

Fig. 6. Solubility surface in the system acetic acid—*n*-propanol—water—*n*-propyl acetate at 293.15 K.

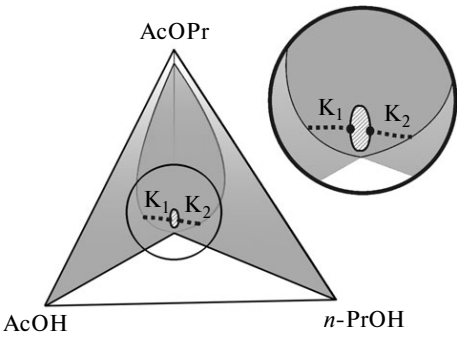

Fig. 7. Region of intersection of the chemical equilibrium surface and binodal surface in the system acetic acid—*n*-propanol—water—*n*-propyl acetate at 293.15 K (hatched): chemical equilibrium in the heterogeneous system (the critical curve of the liquid—liquid equilibrium is dotted); K_1 and K_2 are the points corresponding to the critical phases in the chemically equilibrium states. The magnified fragment of the diagram is also presented: the critical curve and the region of chemically equilibrium layering solutions.

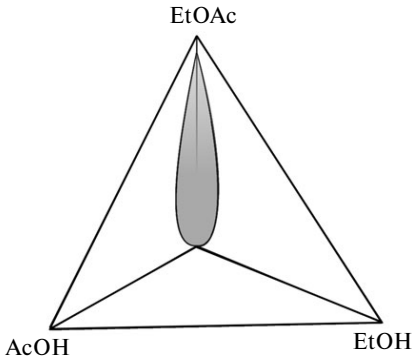

Fig. 8. Layering surface in the acetic acid—ethanol—water—ethyl acetate system at 293.15 K.

surfaces and the region of their intersection (compositions of the layering chemically equilibrium mixture) are presented in Fig. 7 along with the experimentally determined[48—50] curve of critical compositions of the liquid—liquid equilibrium. The curve also passes through the region of simultaneously chemical and phase equilibrium. Two points at the boundary of this region correspond to the critical phases of the liquid—liquid equilibrium also existing in the chemically equilibrium states. All other points in the critical curve belong to the states at chemical nonequilibrium.

Figure 8 presents the layering region for the acetic acid—ethanol—water—ethyl acetate system at 293.15 K constructed according to published data.[60] The shape of this region is similar to that for the system acetic acid—*n*-propanol—water—*n*-propyl acetate. The chemically equilibrated surfaces[60] are also arranged similarly to the diagrams in Figs 3 and 5. However, in the case of the system of ethyl acetate synthesis, no intersections of the considered thermodynamic surfaces were observed.

The ternary diagrams in Figs 5—7 mainly provide the qualitative description of the phase structure. As outlined above, the transformed concentration variables (α variables) allow one to present the properties of the system on the chemical equilibrium surface as binary diagrams. Figure 9 presents the boundaries of the layering region of the chemically equilibrium mixture acetic acid—*n*-propanol—water—*n*-propyl acetate at 313.15 K in the square of α variables and the both points of compositions of the chemically equilibrium critical phases.

The region of simultaneous chemical and phase equilibrium is an analog of the "unique reactive tie-line" in ternary systems. This region can be considered as a continuous set of tie-lines, each of which connects two points of liquid—liquid equilibrium simultaneously belonging to the chemical equilibrium surface.

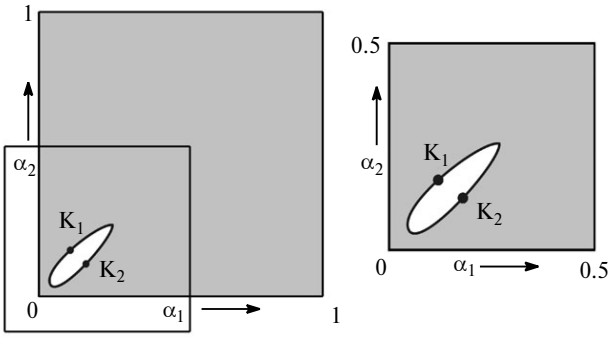

Fig. 9. Layering boundaries of the chemically equilibrium system acetic acid—*n*-propanol—water—*n*-propyl acetate at 293.15 K in the square of α variables; K_1 and K_2 are the points corresponding to the critical phases in the chemically equilibrium states. The magnified fragment of the diagram is also presented.

Displacement of chemical and phase equilibria

The conditions of chemical equilibrium and its stability is a well developed area of chemical thermodynamics.[15—17,24] The problem of displacement of chemical equilibrium in a homogeneous system with changing temperature and pressure was also considered in numerical thermodynamic studies. The problem of displacement of chemical equilibrium accompanied by phase transitions or the issue of displacement of phase equilibrium in a system with chemical interaction of components was also addressed.[15,16] Therefore, in this Section we discuss only some aspects of thermodynamic analysis of displacement of equilibrium in complicated systems in which chemical and phase processes can occur simultaneously. The main attention is given to alternative approaches based on the results of the thermodynamic theory of stability.

Let us designate the intensive and extensive combined thermodynamic parameters, including the amounts and chemical potentials of the substances that do not participate in the chemical reaction, by symbols X_i and Y_i, respectively. Standard designations m_i and μ_i will be retained for participants of the reaction, and the system will be accepted closed for reactants. For any pair of parameters X_i and Y_i, the following equation is valid:[61—63]

$$\left(\frac{\partial X_1}{\partial Y_1}\right)_{\sum_i \nu_i\mu_i} = \left(\frac{\partial X_1}{\partial Y_1}\right)_{\xi} + \left(\frac{\partial X_1}{\partial \xi}\right)_{Y_1}\left(\frac{\partial \xi}{\partial Y_1}\right)_{\sum_i \nu_i\mu_i}, \qquad (13)$$

where ξ is the chemical variable, whose subscript implies that the reaction does not occur or stopped; subscript $\sum_i \nu_i\mu_i$ indicates that affinity $A = -\sum_i \nu_i\mu_i$ has a constant value, in particular, for chemical equilibrium $\sum_i \nu_i\mu_i = 0$. Since the numeration of thermodynamic variables is arbitrary, Eq. (13) refers to the "first" pair of combined extensive and intensive parameters X_1 and Y_1, which does not prevent us to draw more general conclusions. Due to the thermodynamic correlations of reciprocity and stability conditions, the second term in the right-hand part of Eq. (13) is negative and, hence, the following inequality[62] is valid:

$$0 < \left(\frac{\partial X_1}{\partial Y_1}\right)_{\sum_i \nu_i\mu_i} < \left(\frac{\partial X_1}{\partial Y_1}\right)_{\xi}, \qquad (14)$$

or, for reciprocal derivatives,

$$\left(\frac{\partial Y_1}{\partial X_1}\right)_{A} > \left(\frac{\partial Y_1}{\partial X_1}\right)_{\xi} > 0, \qquad (15)$$

where index $\sum_i \nu_i\mu_i$ is replaced by the identical one, in this case, by index A (affinity constancy). Note that condition implying that ζ = const in the system closed for reactants is equivalent to the composition constancy. The affinity constancy (A = const) means that the composition can vary, for example, under the condition $A = 0$, the equilibrium can displace due to changing the external conditions; *i.e.*, the reaction occurs until new equilibrium is attained. From this follows a general conclusion concerning derivatives $\partial Y_1/\partial X_1$: at a constant composition the value of the extensive parameter derivative with respect to the combined intensive parameter is lower than the same value for the chemical transformation at equilibrium. The difference between these derivatives has a finite value and can be calculated if the values in the second term of the right-hand part of Eq. (13) are known. Note that symbols X_i and Y_i for the amounts of substances and their chemical potentials are referred only to the substances that do not participate in the chemical reaction.

Here we will not consider how to derive equations for several chemical reactions[61—63] and will discuss only the result: a sequence of inequalities reflecting the difference between the derivatives. In the case of s independent reactions, the difference between derivatives $\left(\partial X_1/\partial Y_1\right)$ is determined by the number of chemical equilibria

$$\left(\frac{\partial X_1}{\partial Y_1}\right)_{\xi_1,\xi_2,\ldots,\xi_s} > \left(\frac{\partial X_1}{\partial Y_1}\right)_{A_1,\xi_2,\xi_3,\ldots,\xi_s} > \ldots$$

$$\ldots > \left(\frac{\partial X_1}{\partial Y_1}\right)_{A_1,A_2,\xi_3,\ldots,A_{s-1},\xi_s} > \left(\frac{\partial X_1}{\partial Y_1}\right)_{A_1,A_2,\ldots,A_s} > 0, \qquad (16)$$

where subscripts indicate the constancy of the affinity or chemical variable. The first of the derivatives is taken under the conditions that all chemical reactions are inhibited. The latter derivative means that the affinity constancy of all reactions is maintained; in particular, at all $A = 0$ the complete chemical equilibrium is observed for all reactions. Other derivatives correspond to intermediate cases of incomplete chemical equilibrium.

A similar sequence of inequalities can be written for phase equilibria. In this case, partial equilibrium can be considered. For example, in the two-phase n-component system in which all extensive parameters, except for the "first" one is maintained (the numeration of the derivatives is again arbitrary), the following equation is valid[2,62,64] for processes changing the states of the phase:

$$\left(\frac{\partial X_1}{\partial Y_1}\right)_{Y_2^{(1)},Y_3^{(1)},\ldots,Y_{n+2}^{(1)}} > \left(\frac{\partial X_1}{\partial Y_1}\right)_{(X_2^{(1)}-X_2^{(2)}),Y_3^{(1)},\ldots,Y_{n+2}^{(1)}} > \ldots$$

$$\ldots > \left(\frac{\partial X_1}{\partial Y_1}\right)_{X_2^{(1)}-X_2^{(2)},\ldots,(X_n^{(1)}-X_n^{(2)}} > 0,$$

$$Y_2,\ Y_3,\ldots,\ Y_{n+2} = \text{const}, \qquad (17)$$

where symbols without superscripts refer to the heterogeneous system as a whole. Condition $Y_i^{(1)}$ = const (at Y_i = const) indicates the absence of the phase transition for parameter i. Condition $X_i^{(1)} - X_i^{(2)}$ = const implies the possibility of the corresponding phase transition, in particular, at $X_i^{(1)} - X_i^{(2)} = 0$, and the existence of processes that maintain the phase equilibrium relative to parameter i (partial equilibrium). From Eq. (17) at $Y_2,\ Y_3,\ldots,\ Y_{n+2}$ = = const it follows that

$$\left(\frac{\partial Y_1}{\partial X_1}\right)_{(X_2^{(1)}-X_2^{(2)})=0,\ldots,(X_{n+2}^{(1)}-X_{n+2}^{(2)})=0} > \ldots$$

$$\ldots > \left(\frac{\partial Y_1}{\partial X_1}\right)_{Y_2^{(1)},Y_3^{(1)},\ldots,Y_{n+2}^{(1)}} > 0. \qquad (18)$$

This inequality gives a partial result similar to the above-presented one for chemical processes: the derivative of the extensive parameter with respect to the combined intensive parameter at a constant composition is lower than the same value at equilibrium transformation in the heterogeneous system. Similar conclusions were discussed in the work dealing with the analysis of stability, the moderation theorems, and the Le Chatelier—Braun principle.[16] Thus, both chemical and equilibrium phase transformations in a heterogeneous system give the same results: the value of derivative $\left(\partial X_1/\partial Y_1\right)$ is higher than the same derivative for the process at a constant composition. Note that the above presented discussion of phase and chemical displacement can be performed on a common basis by introducing a generalized concept on affinity of both chemical and phase processes.[16,61—63,65]

Other forms of thermodynamic inequalities characterizing thermodynamic displacement[66] and various aspects of thermodynamic description of heterogeneous systems with chemical reactions in the liquid phase are also described.[10,67]

The results discussed in this section were presented in the general form. Now let us present them more clearly using specific thermodynamic values. Note that we confine our consideration to variables in the fundamental Gibbs equation, *i.e.*, intensive parameters T, $(-P)$, $\mu_j \equiv X_i$ and extensive parameters S, V, $m_j \equiv Y_i$. Then, for the entropy and absolute temperature we have

$$\left(\frac{\partial S}{\partial T}\right)_A > \left(\frac{\partial S}{\partial T}\right)_\xi > 0$$

and, correspondingly, for the heat capacity at constant pressure or temperature we obtain

$$c_{p,A} > c_{p,\xi} > 0 \text{ or } c_{V,A} > c_{V,\xi} > 0.$$

These conditions (for constant chemical affinity A) coincide with the known result for equilibrium, *i.e.* $A = 0$: the heat capacity at a constant composition is always lower than the heat capacity at equilibrium transformation.[16] The same conclusion follows from condition (18) not only for the chemical but also for phase equilibrium: if the equilibrium phase transition is possible in the system, then the heat capacity is higher than that in the absence of the equilibrium phase transition.

For isothermic or isoentropic compressibility when

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S,$$

we also obtain from Eq. (15)

$$\kappa_{T,A} > \kappa_{T,\xi} > 0 \text{ or } \kappa_{S,A} > \kappa_{S,\xi} > 0;$$

this result for equilibrium ($A = 0$) was also discussed.[16] For the phase equilibrium inequality (18) gives the same result. In the case of derivatives $\partial\mu_j/\partial m_j$ (for substances that do not participate in the reaction, for example, for the solvent), the result of analysis of the corresponding inequalities, *e.g.*,

$$\left(\frac{\partial m_j}{\partial \mu_j}\right)_A > \left(\frac{\partial m_j}{\partial \mu_j}\right)_\xi > 0, \qquad (19)$$

seems less clear; however, they allow one to draw a practically important conclusion. Using the known equation for chemical potentials

$$\mu_j = \mu_j^0(T) + RT\ln p_j,$$

where p_j is the partial pressure of substance j, inequalities (19) can be transformed into the following form:

$$\left(\frac{\partial p_j}{\partial m_j}\right)_\xi > \left(\frac{\partial p_j}{\partial m_j}\right)_A > 0.$$

This inequality suggests that the addition of an inert solvent to the chemically reacting mixture results in an

increase in its partial pressure, and once the chemical equilibrium is ataained the partial pressure somewhat decreases. In the case of phase equilibration, a similar result was observed in a series of works.[22,61,62]

The considered particular cases of thermodynamic regularities of displacement of equilibrium in heterogeneous systems and an analysis of the diagrams describing occurrence of phase and chemical equilibrium simultaneoulsy illustrate a complicated character of the behavior of the physicochemical system with multiple processes (chemical and phase) proceeding in a heterogeneous system. In the thermodynamic study of similar system one should take into account not only lines and surfaces of phase and chemical equilibria, but also additional units of the diagrams, such as reactive lines and curves (surfaces) of constant chemical affinity. A lack of experimental thermodynamic information on chemical processes in liquid phase systems with layering seems evident. In addition, a complex thermodynamic kinetic approach using, in particular, experimental data on rates of phase transitions and simultaneously occurring chemical reactions seems necessary. The development of studies in this direction is obviously promising with respect to both the search for new physicochemical regularities and practical applications in the field of technology of reactive mass exchange processes.

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